

THE CONSTITUENTS OF
THE ESSENTIAL OIL OF
CALIFORNIAN LAUREL

BY

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LXIII.—*The Constituents of the Essential Oil of Californian Laurel.*

By FREDERICK BELDING POWER and FREDERIC HERBERT LEES.

THE Californian laurel, *Umbellularia Californica* (Nuttall), is a handsome, evergreen tree, which is distributed from the valleys of Oregon through the California coast ranges and along the high western slopes of the Sierra Nevada to the southern slopes of the San Bernardino Mountains (compare "The Silva of North America," by Charles Sprague Sargent, vol. vii, pp. 19—22, tab. cccvi.). It is also known under the names of "mountain laurel," "cajeput," "spice tree," "California olive," "California bay-tree," and "pepper-wood." *

* The name of "pepper-wood" has also been given to a species of *Xanthoxylum*.

The essential oil, which is distilled from the leaves,* has been described as having a pale yellow colour, and a pungent, aromatic odour, resembling that of a mixture of nutmeg and cardamom. When inhaled in any considerable amount, it attacks the mucous membranes, produces headache, and excites a flow of tears ("Die aetherischen Oele," by Gildemeister and Hoffmann, p. 527).

The only chemical examination hitherto made of this oil which requires notice is that by Stillman (*Ber.*, 1880, 13, 629, and *Amer. Chem. J.*, 1880, 2, 38), who obtained by its fractional distillation two principal fractions, boiling respectively at 167—168° and 215—216°. The fraction 167—168° was regarded by Stillman as having the formula $C_{20}H_{32}H_2O$, and as corresponding with the "terpinol" of Wiggers, which, however, has since been shown to be a mixture of several substances. To the fraction 215—216°, which he observed to possess the pungency characteristic of the original oil, was assigned the formula $C_8H_{12}O$ and the name of "umbellol," but without any determination of its chemical nature. From the results of our investigation, it is evident that both of the fractions analysed by Stillman consisted of a mixture of substances.

EXPERIMENTAL.

The oil employed in this investigation (1200 grams), which was specially distilled for us in California, and was therefore perfectly genuine, had a pale yellow colour, and an odour which at first was agreeably aromatic and somewhat camphoraceous, but, as has previously been noticed, when strongly inhaled it is exceedingly pungent, affecting particularly the mucous membranes of the nose and eyes. Its sp. gr. was 0.9483 at 16°/16°, and its optical rotatory power -22° in a 100 mm. tube. The oil was completely soluble in 1.5 parts of 70 per cent. alcohol; it formed no solid compound with sodium hydrogen sulphite. As it was thought that it might contain sulphur or nitrogen compounds, special tests were made for these elements, but with negative results.

A determination of the amount of free acids and of esters gave the following data: 10.35 grams of the oil required 1.5 c.c. of a seminormal alcoholic solution of sodium hydroxide to neutralise the free acids. On subsequently adding an excess of the alkali solution and boiling, it was found that only 0.8 c.c. was required to hydrolyse the esters present. These, if calculated as $C_{10}H_{17} \cdot C_2H_3O_2$, would therefore only amount to 0.8 per cent. It was observed that, on boiling the oil with

* Schimmel & Co., in the appendix to their *Bericht* for October, 1887, p. 47, have recorded a yield of 7.6 per cent. of essential oil from the leaves of Californian laurel, and others have noted yields varying between 2.5 and 4 per cent.

an excess of an alcoholic solution of sodium hydroxide, its pungent odour was not destroyed.

The separation of the small amount of uncombined acids was effected by shaking the oil four times with dilute aqueous sodium carbonate and finally with water. The combined aqueous liquids, after shaking with ether to remove adhering oil, were evaporated to a small volume, acidified with sulphuric acid, and distilled in steam. From the distillate, ether extracted 2·3 grams of a light yellow, somewhat pungent, oily acid, which was converted through the ammonium salt into a silver salt. The latter formed a dense, white, amorphous precipitate, and was obtained in two fractions, which were analysed :

(a) 0·1523 gave 0·0495 Ag. $\text{Ag} = 32\cdot5$.

(b) 0·1277 „ 0·0599 Ag. $\text{Ag} = 46\cdot9$ per cent.

The aqueous liquid from which the oily acids had been extracted still contained an acid, which was converted into its barium salt. This was crystalline, but, in attempting to prepare the corresponding silver salt, the dense, white precipitate first produced almost immediately became reduced. Another portion of the barium salt gave a precipitate of calomel with a solution of mercuric chloride. The oil thus evidently contains an exceedingly small amount of formic acid, associated with a mixture of some higher fatty acids.

Identification of Eugenol.

The whole of the oil, after the removal of the fatty acids, was shaken six times with 5 per cent. aqueous potassium hydroxide, and finally several times with water. The combined alkaline liquids were then shaken with ether to remove adhering oil, and acidified with sulphuric acid, when a quantity of an oily liquid separated ; this was taken up with ether, the ethereal solution washed, dried, and the ether removed. The residual oil, amounting to 20 grams, was then distilled under 80 mm. pressure, when it passed over completely between 170° and 175° , but principally at 170 — 172° . A fraction collected at the latter point was analysed :

0·1106 gave 0·2964 CO_2 and 0·0749 H_2O . $\text{C} = 73\cdot1$; $\text{H} = 7\cdot5$.

$\text{C}_{10}\text{H}_{12}\text{O}_2$ requires $\text{C} = 73\cdot2$; $\text{H} = 7\cdot3$ per cent.

It gave a blue coloration with ferric chloride, and afforded a benzoyl derivative, which, after crystallisation from alcohol, melted at 69 — 70° . It is thus shown that the oil contains an appreciable amount of eugenol.

Fractional Distillation of the Oil.

The whole of the oil remaining from the foregoing treatment was mixed with a quantity of ether and dried with calcium chloride. After the removal of the ether, the residual oil was first distilled under the ordinary pressure until the temperature had reached 207° , and then under diminished pressure. In this way, a small amount of dark, non-volatile matter was removed. The whole of the distilled oil was then subjected to a prolonged series of fractional distillations under the ordinary pressure, when a number of fractions were obtained boiling between the following ranges of temperature: $150-165^{\circ}$; $165-169^{\circ}$; $169-173^{\circ}$; $173-175^{\circ}$; $175-180^{\circ}$; $180-185^{\circ}$; $185-195^{\circ}$; $195-205^{\circ}$; $205-215^{\circ}$; $215-217^{\circ}$; $217-222^{\circ}$; $222-227^{\circ}$; $227-235^{\circ}$; $235-245^{\circ}$; $245-250^{\circ}$.

Identification of Pinene.

Fraction $150-165^{\circ}$ (sp. gr. = 0.8659 at $16^{\circ}/16^{\circ}$; $\alpha_D - 20^{\circ}$ in a 100 mm. tube).—This was a colourless, limpid liquid, having a terpene-like odour, and was practically insoluble in 70 per cent. alcohol.

0.1491 gave 0.4672 CO_2 and 0.1567 H_2O . $\text{C} = 85.5$; $\text{H} = 11.7$.

$\text{C}_{10}\text{H}_{16}$ requires $\text{C} = 88.2$; $\text{H} = 11.8$ per cent.

This fraction, which evidently consisted chiefly of a hydrocarbon, associated with a small amount of an oxygenated substance which could not be eliminated by fractional distillation, was shown to contain *l*-pinene by the formation of a crystalline nitrosecchloride, from which were prepared the nitrolpiperidine and nitrolbenzylamine, melting respectively at $119-120^{\circ}$ and $124-125^{\circ}$.

Fraction $165-169^{\circ}$ (sp. gr. = 0.8770 at $16^{\circ}/16^{\circ}$; $\alpha_D - 18^{\circ}20'$ in a 100 mm. tube).—This fraction had an odour recalling that of pinene, but was also somewhat camphoraceous; it consisted principally of pinene, but contained more of the oxygenated substance than the preceding fraction.

Fraction $169-173^{\circ}$ (sp. gr. = 0.8903 at $16^{\circ}/16^{\circ}$; $\alpha_D - 13^{\circ}12'$ in a 100 mm. tube).—This fraction had a more highly camphoraceous odour than the preceding fraction; it was specially tested for phellandrene, but with a negative result.

Fraction $173-175^{\circ}$.—This was relatively small in amount.

Identification of Cineol.

Fraction 175—180° (sp. gr. = 0.9092 at 16°/16°; $\alpha_D - 3^\circ 30'$ in a 100 mm. tube).—This very large fraction was a colourless liquid, possessing the characteristic, camphoraceous odour of cineol.

0.1144 gave 0.3381 CO₂ and 0.1205 H₂O. C = 80.6; H = 11.7.

C₁₀H₁₈O requires C = 77.9; H = 11.7 per cent.

This fraction evidently consisted principally of an oxygenated substance, associated with only a small proportion of a hydrocarbon. With tetraiodopyrrole it afforded the crystalline, double compound of cineol, C₁₀H₁₈O, C₄I₄NH, which melted at 115° with decomposition (Hirschsohn, *Pharm. Zeit. Russ.*, 1893, 32, 49, 67). Cineol hydrobromide was accordingly prepared by saturating a cooled solution of the fraction in light petroleum with hydrogen bromide, and then decomposed with sodium carbonate, when the regenerated cineol* was recognised by its physical properties and by analysis:

0.1293 gave 0.3672 CO₂ and 0.1368 H₂O. C = 77.5; H = 11.8.

C₁₀H₁₈O requires C = 77.9; H = 11.7 per cent.

Sp. gr. = 0.9276 at 16°/15°. Optically inactive.

Limonene and dipentene were also sought for in this fraction by attempting to form their respective crystalline tetrabromides, but only an oily bromo-compound resulted, which did not become crystalline even after several days.

Fractions 180—185° and 185—195°.—These two fractions were relatively very small in amount. They had a pronounced odour of cineol, and evidently consisted of that substance together with a small amount of the constituents of the fractions of higher boiling point.

Fraction 195—205° (sp. gr. = 0.9308 at 15°/15°; $\alpha_D - 22^\circ 48'$ in a 100 mm. tube).—This was a very small fraction.

0.1036 gave 0.3015 CO₂ and 0.1012 H₂O. C = 79.4; H = 10.9.

0.1020 „ 0.2978 CO₂ and 0.0990 H₂O. C = 79.6; H = 10.8 per cent.

It had the odour of the preceding fractions containing cineol and also the peculiar pungency of a fraction of higher boiling point. It was specially tested for linalool by the oxidation of 5 grams of the liquid

* The presence of cineol in this oil appears to have first been observed by Schimmel & Co., since, in the appendix to their *Bericht* of October, 1893, p. 27, and also of April, 1897, p. 31, it is recorded as the only known constituent of the oil. This has been overlooked in the notice of the oil given in "Die aetherischen Oele," by Gildemeister and Hoffmann, p. 527.

with chromic acid, but no evidence of the formation of citral was obtained.

Fraction 205—215° (sp. gr. = 0.9460 at 15°/15°; $\alpha_D - 30^\circ 3'$ in a 100 mm. tube).—This fraction, which was comparatively small, had a very pungent odour, and did not differ very essentially from the large, principal fraction collected at 217—222°.

0.1036 gave 0.3011 CO₂ and 0.0944 H₂O. C = 79.2; H = 10.1.

0.0870 „ 0.2510 CO₂ „ 0.0810 H₂O. C = 78.7; H = 10.3 per cent.

Although these results indicated that this fraction consisted principally of the constituent of the large fraction boiling at 217—222°, the possibility of the presence of a small amount of camphor or of borneol was not precluded. In order to test for these two substances, 10 grams of the liquid were oxidised by warming for half an hour on a water-bath, with occasional vigorous shaking, with a solution of 80 grams of potassium dichromate and 120 grams of sulphuric acid in 200 c.c. of water. During the oxidation, the odour of camphor did not become apparent, and on subsequently diluting the mixture with water and distilling in steam no camphor was found in the distillate.

Fraction 215—217° (sp. gr. = 0.9546 at 15.5°/15°; $\alpha_D - 34^\circ 35'$ in a 100 mm. tube).—These and other characters afforded evidence that this consisted to a very large extent of the constituent of the following fraction.

Isolation of a New Ketone, Umbellulone, C₁₀H₁₄O.

Fraction 217—222° (sp. gr. = 0.9614 at 15.5°/15°; $\alpha_D - 36^\circ 33'$ in a 100 mm. tube).—This fraction, which was the largest obtained and contained the most interesting constituent of the oil, was colourless, had a somewhat mint-like odour, and possessed in a high degree the peculiar pungency characteristic of the original oil.

0.1144 gave 0.3309 CO₂ and 0.1014 H₂O. C = 78.9; H = 9.9 per cent.

During the distillation of this large fraction, it was observed that the most constant boiling point was 218° (752 mm.). A quantity collected at this point was also analysed, and the physical constants determined:

0.1226 gave 0.3566 CO₂ and 0.1078 H₂O. C = 79.3; H = 9.8.

0.0958 „ 0.2780 CO₂ „ 0.0847 H₂O. C = 79.1; H = 9.8 per cent.

Sp. gr. = 0.9584 at 15°/15°; $\alpha_D - 37^\circ$ in a 100 mm. tube.

From these data, and from a consideration of the analytical figures and physical constants of the smaller fractions boiling below the fraction 217—222°, it seemed evident that this consisted mainly of a substance

having the formula $C_{10}H_{14}O$, which requires $C=80.0$; $H=9.3$ per cent. The substance readily interacted with semicarbazide and hydroxylamine respectively, but did not respond to Schiff's rosaniline test for aldehydes; it is, therefore, a ketone. Among all the ketones which have hitherto been isolated from essential oils, none has the peculiar and extreme pungency of this substance, and there is only one of the naturally occurring ketones, namely, carvone, with which it is isomeric. Furthermore, a study of its behaviour towards many reagents has shown that it is not identical with any of the ketones hitherto described. We have, therefore, in consideration of its botanical source, given it the designation of *umbellulone*.

Umbellulone does not combine with sodium hydrogen sulphite, nor does it, like its isomeride, carvone, form a compound with hydrogen sulphide. It combines directly with two atomic proportions of bromine in the cold, and readily decolorises a cold solution of potassium permanganate. It, therefore, would seem to contain only one ethylenic linking, and, since it has the formula $C_{10}H_{14}O$, would appear to be a cyclic ketone with two closed rings. Its behaviour towards semicarbazide and hydroxylamine is abnormal, inasmuch as under the usual conditions these bases not only interact with the carbonyl group with the elimination of water to form a semicarbazone and oxime respectively, but at the same time their elements become attached to the two carbon atoms of the ethylenic linking. This behaviour of certain unsaturated open chain and closed ring ketones has previously been observed by Harries and his pupils (*Ber.*, 1897, 30, 230), by Tiemann (*Ber.*, 1897, 30, 251, and 1900, 33, 562), and more recently, with regard to the action of semicarbazide, by Rupe and Schlochoff (*Ber.*, 1903, 36, 4377).

Semicarbazidodihydroumbellulonesemicarbazone,
 $C_{10}H_{15}(\cdot N \cdot NH \cdot CO \cdot NH_2) \cdot CH_4ON_3$,
and the Regeneration of Pure Umbellulone, $C_{10}H_{14}O$.

To a solution in the minimum amount of water of a large excess of semicarbazide hydrochloride (40 grams) and sodium acetate (50 grams) were added umbellulone (20 grams) and just sufficient methyl alcohol to form a clear solution. After three days, during which interval nothing separated, a quantity of water was added, which caused the deposition of a bulky, white, crystalline substance. This was collected and drained at the pump, and then washed well with water in order to remove the uncombined ketone, since it was found that after the first two days the reaction proceeds very slowly, and the yield of product therefore never greatly exceeded 50 per cent. of the calculated amount. As thus obtained, the compound melted at 216° with

evolution of gas, and was practically pure. It was recrystallised from ethyl alcohol, when it separated almost completely from the cooled solution in compact rosettes of fine needles, which melted at 217° with evolution of gas.

0.1751 gave 0.3276 CO_2 and 0.1260 H_2O . $\text{C} = 51.0$; $\text{H} = 8.0$.

0.1222 „ 0.2288 CO_2 „ 0.0885 H_2O . $\text{C} = 51.1$; $\text{H} = 8.0$ per cent.

It is readily soluble in hot water, without decomposition, and on cooling it separates in small, transparent, cubical crystals, which melt at 217° with evolution of gas.

0.1128 gave 0.2120 CO_2 and 0.0810 H_2O . $\text{C} = 51.2$; $\text{H} = 8.0$.

0.1268 „ 32.2 c.c. moist nitrogen at 22° and 766 mm. $\text{N} = 29.0$.

$\text{C}_{12}\text{H}_{22}\text{O}_2\text{N}_6$ requires $\text{C} = 51.1$; $\text{H} = 7.8$; $\text{N} = 29.8$ per cent.

Semicarbazidodihydroumbellulonesemicarbazone is soluble in dilute mineral acids, and, on warming the solutions, it is decomposed, regenerating umbellulone in quantitative yield. This process has been utilised in order to prepare a pure specimen of the ketone for the determination of its physical constants.

A quantity of the semicarbazidosemicarbazone, mixed with about 500 c.c. of water and sufficient sulphuric acid added to effect decomposition, was distilled in steam ; the umbellulone contained in the distillate was extracted with ether, the ethereal solution dried with calcium chloride, and the ether removed. The residual liquid was then distilled, when it was found to boil at $219\text{--}220^{\circ}$ (corr.) under 749 mm. pressure. It is a perfectly colourless liquid, the odour of which is at first pleasant, somewhat resembling that of mint, but when more strongly inhaled is exceedingly pungent, producing the effects already described.

0.1634 gave 0.4778 CO_2 and 0.1370 H_2O . $\text{C} = 79.7$; $\text{H} = 9.3$.

0.1400 „ 0.4083 CO_2 „ 0.1195 H_2O . $\text{C} = 79.5$; $\text{H} = 9.5$.

$\text{C}_{10}\text{H}_{14}\text{O}$ requires $\text{C} = 80.0$; $\text{H} = 9.3$ per cent.

Sp. gr. = 0.9581 at $15^{\circ}/15^{\circ}$; $[\alpha]_{\text{D}} - 37^{\circ}$.

Hydroxylaminodihydroumbelluloneoxime, $\text{C}_{10}\text{H}_{15}(\text{:N}\cdot\text{OH})\cdot\text{NH}\cdot\text{OH}$.

Umbellulone (15 grams) was added to a solution of hydroxylamine (four molecular proportions), formed by adding a solution of sodium methoxide in methyl alcohol (9.2 grams Na in 300 c.c. methyl alcohol) to a solution of hydroxylamine hydrochloride (28 grams) in the same solvent (300 c.c.). The mixture was then boiled for two hours. After removing the methyl alcohol completely by distillation, the residue, consisting of the product of the reaction mixed with sodium

chloride, was mixed with water and the undissolved viscid oil extracted with ether, the ethereal liquid being then washed, dried, and distilled to remove the solvent. The product, which weighed 18 grams, was a clear, nearly colourless liquid of a honey-like consistency.

In order to remove a small amount of substance which had not been converted into oxime, the product was mixed with dilute sulphuric acid, in which the hydroxylamino-oxime is readily soluble, and the small amount of non-basic matter which remained as an oil was then removed by extraction with ether. By the addition of sodium carbonate to the acid aqueous liquid, the base was again set free; it was then extracted with ether, dried, and the ether removed by distillation on the water-bath and by subsequently exposing the substance in a vacuum-desiccator over paraffin wax. The base was thus obtained as a hard, slightly green, glistening, amorphous substance, which could readily be powdered; it has thus far not been possible to obtain it in a definite crystalline form.

0.2035 gave 23.2 c.c. moist nitrogen at 23° and 768 mm. $N = 13.0$.

$C_{10}H_{18}O_2N_2$ requires $N = 14.1$ per cent.

Although the percentage of nitrogen obtained is somewhat less than that required by theory for the pure substance, the result is sufficiently conclusive to show its composition, inasmuch as the normal oxime, $C_{10}H_{14}:N \cdot OH$, would require $N = 8.5$ per cent. The discrepancy is in all probability due to the product containing a small amount of hydroxylaminodihydroumbellulone, $C_{10}H_{15}O \cdot NH \cdot OH$, which would not only be more readily formed than the normal oxime, but would be markedly basic, and therefore more likely to be present than the latter, which, on account of its feebly basic properties, would be readily removed by ether from a solution of the product in dilute acids (compare Harries, *loc. cit.*, and Tiemann, *loc. cit.*).

Hydroxylaminodihydroumbelluloneoxime very closely resembles diacetonehydroxylamine (*Ber.*, 1898, 31, 1376), hydroxylaminodihdropulegone (pulegonehydroxylamine, *ibid.*, 1809), and hydroxylaminodihydrocarvoxime (oxaminocarvoxime, *ibid.*, 1810). It is readily soluble in dilute alkali hydroxides and also in dilute acids, forming salts. Its solution in aqueous sodium hydroxide reduces Fehling's solution with extraordinary readiness, even in the cold.

Fraction 222—227° (sp. gr. = 0.9842 at 15°/15°; $n_D - 29^\circ 17'$ in a 100 mm. tube).—This was a comparatively small fraction, which had a pronounced odour of umbellulone and a faint one of safrole; it consisted chiefly of umbellulone, with smaller amounts of the constituents of the following fractions.

Identification of Safrole.

Fraction 227—235° (sp. gr. = 0.9976 at 15°/15°; $\alpha_D - 20^\circ 27'$ in a 100 mm. tube).—This fraction, which was somewhat larger than the preceding one, was slightly pungent, but at the same time possessed the unmistakable odour of safrole.

While distilling this fraction it was observed that it boiled most constantly at 230—231°. A small amount was therefore separately collected at this point for analysis and the determination of its physical constants :

0.0851 gave 0.2411 CO₂ and 0.0680 H₂O. C = 77.3 ; H = 8.9 per cent.

Sp. gr. = 0.9930 at 16°/16°; $\alpha_D - 25^\circ 4'$ in a 100 mm. tube.

In order to confirm the above indication of the presence of safrole, and at the same time to ascertain whether geraniol was present, 10 grams of the liquid were oxidised by warming gently on a water-bath, with occasional shaking, with a solution of 50 grams of potassium dichromate and 16 grams of sulphuric acid in 160 c.c. of water. The brown oily product, when isolated by extraction with ether, had the odour of piperonal, but not of citral ; it was vigorously shaken with a saturated solution of sodium hydrogen sulphite, when, after some time, a crystalline compound separated, which was collected, washed with ether, and decomposed with a dilute solution of sodium hydroxide. The small amount of liberated oil which was extracted with light petroleum became crystalline on introducing a trace of piperonal. The crystals melted at 35°, and had the characteristic odour of piperonal. It was thus shown that the essential oil contains safrole, but only in very small amount.

Fraction 235—245° (sp. gr. = 1.013 at 15°/15°; $\alpha_D - 8^\circ 40'$ in a 100 mm. tube).—This fraction was equal in amount to the preceding, and it had the odour of safrole. During its distillation, a small amount was separately collected at 240°, when the temperature was most constant. This was analysed and its physical constants determined :

0.0846 gave 0.2361 CO₂ and 0.0664 H₂O. C = 76.1 ; H = 8.7 per cent.

Sp. gr. = 1.009 at 16°/16°; $\alpha_D - 11^\circ 41'$ in a 100 mm. tube.

This fraction consisted to a large extent of the constituent of the following fraction.

Identification of Eugenol Methyl Ether.

Fraction 245—250° (sp. gr. = 1.021 at 16°/16°; $\alpha_D - 2^\circ 22'$ in a 100 mm. tube).—This was a large fraction, which had a slightly yellow

colour and was nearly odourless. The greater portion was observed to boil at 248—250°, and a quantity was therefore separately collected at this point for the purpose of analysis and the determination of its physical constants :

0.1035 gave 0.2846 CO₂ and 0.0796 H₂O. C = 75.0 ; H = 8.5.

C₁₁H₁₄O₂ requires C = 74.2 ; H = 7.9 per cent.

This fraction was shown to consist of eugenol methyl ether by the fact that it readily afforded an excellent yield of bromoeugenol methyl ether dibromide, C₆H₂Br(O·CH₃)·C₃H₅Br₂, which, after crystallisation from ethyl alcohol, melted at 78—79° (compare Power and Lees, Trans., 1902, 81, 68). Furthermore, on oxidation with potassium permanganate, it yielded veratric acid, melting at 177°.

Summary.

The results of this investigation have shown that the essential oil of Californian laurel contains the following substances :

	Approximate percentage amount.				
1. Eugenol	1.7
2. <i>l</i> -Pinene	6.0
3. Cineol	20.0
4. <i>Umbellulone</i> , C ₁₀ H ₁₄ O	60.0
5. Safrole	A very small amount.		
6. Eugenol methyl ether	10.0
7. A mixture of fatty acids containing formic acid	A very small amount.		

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